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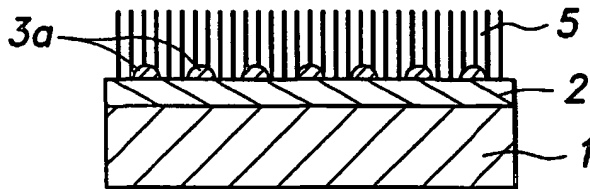
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(54) Title: METHOD FOR MAKING CARBON NANOTUBES



(57) Abstract: In a method for forming a carbon nanotube (5) on an electroconductive member (2), a catalytic layer (3) including a metal or alloy that serves as a catalyst for growing the carbon nanotube is formed on an electroconductive member, the metal or alloy of the catalytic layer is processed so as to turn it into small particles (3a) by heating the catalytic layer formed on the electroconductive member to a prescribed temperature while supplying inert gas, and a carbon nanotube is grown on the

electroconductive member by using the small particles of the metal or alloy of the catalytic layer as a catalyst. The fine metallic particles that can be used as a catalyst for growing the carbon nanotube can be prepared in a simple, economical and efficient manner. The carbon nanotube is highly suitable for use as the diffusion layer of a fuel cell.

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

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This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the International search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the International search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the International search was carried out on the basis of the sequence listing:

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☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

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2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

METHOD FOR MAKING CARBON NANOTUBES

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☒ because this figure better characterizes the invention.

2E _____

☐ None of the figures.

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METHOD FOR MAKING CARBON NANOTUBES

TECHNICAL FIELD

The present invention relates to a method for making carbon film for use in small fuel cells, and in particular to a method for forming a carbon nanotube (CNT) on
5 an electroconductive member.

BACKGROUND OF THE INVENTION

A carbon nanotube consists of a cylindrical tube made of carbon and is provided with a diameter in the order of nanometers owing to certain desirable properties thereof. Japanese patent laid open publication No. 2000-141084, for instance,
10 discloses the use of carbon film consisting of a carbon nanotube as a carrier for platinum or other catalyst. As a carbon nanotube is highly porous, it can serve as a gas diffusion layer. In the invention disclosed in this patent publication, a carbon nanotube film is formed on an iron or nickel film which is in turn formed on an electrode terminal layer made of gold or the like, and a platinum catalyst is sputtered onto the surface of
15 this carbon nanotube film.

There are other methods for forming a carbon nanotube which use electric arc discharge and heating. Japanese patent laid open publication No. 2001-58805, for instance, discloses a method for making carbon nanotube in a large volume and in a simple manner by mixing fullerene molecules with a transition element or an alloy
20 containing a transition element, and heating the mixture on a ceramic board. However, this patent publication contains no mentioning of the formation of a carbon nanotube on an electroconductive member.

It is known to use a transition metal such as iron and nickel in a fine particle form as a catalyst for forming a carbon nanotube. Such fine metallic particles can be
25 prepared by etching metallic film using laser or microwave and filling metallic film into

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the pores of zeolite and porous silicon.

BRIEF SUMMARY OF THE INVENTION

In view of such problems of the prior art, a primary object of the present invention is to provide an improved method for forming a carbon nanotube on an
5 electroconductive member.

A second object of the present invention is to provide a method for forming a carbon nanotube which allows fine metallic particles that can be used as a catalyst for growing a carbon nanotube to be prepared in a simple, economical and efficient manner.

A third object of the present invention is to provide a method for forming a
10 carbon nanotube which is suitable for use in fuel cells.

The present invention accomplishes such objects by providing a method for making a carbon nanotube (5) on an electroconductive member (2), comprising the steps of: forming a catalytic layer (3) including a metal or alloy that serves as a catalyst for growing a carbon nanotube on the electroconductive member; processing the metal
15 or alloy of the catalytic layer so as to turn it into small particles (3a); and growing a carbon nanotube on the electroconductive member by using the small particles of the metal or alloy of the catalytic layer as a catalyst; wherein the step of processing the metal or alloy of the catalytic layer so as to turn it into small particles comprises the step of heating the catalytic layer formed on the electroconductive member to a prescribed
20 temperature while supplying inert gas. Thereby, fine metallic or alloy particles that can be used as a catalyst for growing a carbon nanotube can be prepared in a simple, economical and efficient manner, and a carbon nanotube can be efficiently formed on the electroconductive member by using it as a catalyst.

The catalytic layer may comprise a member selected from a group consisting of
25 Fe, Ni, Co, Mo and an alloy thereof. The electroconductive member may comprise at

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least one material selected from a group consisting of Ti, Au, Ni, Co, Cu, Al, Mo, W and Ta. The inert gas may consist of helium or argon.

The prescribed temperature may be in range of $0.49T_m$ to $0.59T_m$ where T_m is the melting point of the metal or alloy of the catalytic layer in Kelvin. When the catalytic layer is made of iron, the prescribed temperature may be approximately 700 °C. If the heating temperature is higher or lower than this, the particles tend to become coarser, and a desired particle size cannot be obtained. The small particles of the metal or alloy preferably have a particle size of 0.5 to 50 nm. Particles of such a size provides an adequate catalytic action in forming a carbon nanotube, and can be easily obtained by the method described above. By turning the metal or alloy of the catalytic layer into small particles at such a heating temperature, particles of a desired size can be obtained both easily and efficiently.

The step of growing the carbon nanotube may comprise the step of supplying mixed gas containing hydrocarbon gas and the inert gas at a ratio of 1:2 to 1:50 so that amorphous carbon other than a carbon nanotube or soot may be avoided and a carbon nanotube may be formed in an efficient manner without the growth rate thereof being hampered to any great extent.

The step of supplying the mixed gas may be conducted at a flow rate of 1 to 100 cm/min, and more preferably at a flow rate of approximately 30 cm/min. Thereby, the productivity can be improved by controlling the formation of soot and reducing the amount of the material gas that is expelled without contributing to the formation of the carbon nanotube. When the step of growing the carbon nanotube comprises the step of placing the electroconductive member including the small particles of the metal or alloy in a tube having an inner diameter of approximately 30 mm, the flow rate of the mixed gas that is flowed substantially along the length of the tube is preferably in the order of

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200 to 300 sccm (standard cubic centimeter per minute).

The electroconductive member may be deposited on an inorganic substrate made of such material as silicon or glass. The electroconductive member may have a two-layered structure including a titanium (Ti) layer and a tungsten (W) layer formed thereon. Instead of titanium, aluminum (Al), nickel (Ni) or chromium (Cr) can also be used. Instead of tungsten, molybdenum (Mo) or tantalum (Ta) can also be used.

BRIEF DESCRIPTION OF THE DRAWINGS

Now the present invention is described in the following with reference to the appended drawings, in which:

10 Figure 1 is a flowchart describing the preferred embodiment of the method for forming a carbon nanotube film according to the present invention;

Figures 2a to 2e are schematic sectional views illustrating an exemplary method for forming a carbon nanotube film according to the present invention;

15 Figure 3 is a schematic sectional view of the device for forming a carbon nanotube film that can be used for implementing the present invention;

Figure 4a to 4e are schematic sectional views illustrating another exemplary method for forming a carbon nanotube film according to the present invention; and

Figures 5a to 5c are photographs showing the states of iron particles for different processing temperatures.

20 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 is a flowchart of a preferred embodiment of the method of present invention for forming a carbon nanotube, and Figure 2 includes several views showing the states in the various steps of the flowchart of Figure 1.

25 In step 1, an inorganic substrate 1 typically consisting of silicon or glass is cleansed (Figure 2a).

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In step 2, onto the inorganic substrate 1 is deposited an electroconductive layer 2 consisting of a metal such as titanium (Ti), gold (Au), nickel (Ni), cobalt (Co), copper (Cu), aluminum (Al), molybdenum (Mo), tungsten (W), tantalum (Ta), or doped semiconductor material, for instance, by vapor deposition using a resistive heater or sputtering (Figure 2b). When the inorganic substrate 1 consists of silicon, it is preferable to form an electroconductive layer 2 consisting of a two-layered structure including a titanium (Ti) layer formed over the substrate and a tungsten (W) layer formed on the titanium layer. Tungsten is preferred because it has a high melting point and is therefore resistant to the influences of the following thermal processes. Titanium improves the contact between the tungsten layer and substrate, and may be substituted by nickel (Ni), aluminum (Al) or chromium (Cr). Tungsten may be substituted by molybdenum (Mo) or tantalum (Ta). If the inorganic substrate 1 consists of conductive silicon (for instance, doped silicon), it can be advantageously used for conducting electricity to an external circuit.

In step 3, a catalytic layer 3 consisting of a transition metal such as iron (Fe) and capable of a catalytic action for growing a carbon nanotube film is formed on the electroconductive layer 2 (Figure 2c). This can be accomplished by using electron beam vapor deposition. Iron may be substituted by nickel (Ni), cobalt (Co) or molybdenum (Mo). Alternatively, two or more members of a group consisting of iron, nickel, cobalt and molybdenum, or an alloy of such metals can also be used. This combination of the electroconductive layer 2 and catalytic layer 3 formed on the substrate 1 is referred to as an assembly 4 hereinafter.

Figure 3 is a schematic longitudinal sectional view of a preferred device for forming a carbon nanotube on the electroconductive layer 2 by suitably processing the assembly 4 obtained in step 3. This device 10 comprises a quartz tube 12 defining an

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inner bore 30 mm in inner diameter for conducting desired gas along the length thereof. A quartz holder 14 is provided inside this tube 12 for holding the assembly 4 to be processed. The quartz tube 12 is placed in an electric furnace 16 so as to be heated to a desired temperature.

5 Referring to Figure 1 once again, according to the present invention, in step 4, the assembly 4 is secured to the quartz holder 14 in the quartz tube 12, and is heated for a prescribed period of time by suitably adjusting the temperature of the electric furnace 16 while inert gas such as helium and argon is conducted through the quartz tube 12 from an end (left end in Figure 3) thereof at a prescribed velocity. As a result, the metal
10 or alloy of the catalytic layer 3 on the surface of the assembly 4 is turned into fine particles so that a large number of fine particles of the metal or alloy 3a can be obtained (Figure 2d). By thus processing the catalytic layer 3, and obtaining a large number of catalytic particles, the catalytic action during the process of growing the carbon
15 nanotube can be enhanced. If the particles are not fine enough, the direction of the growth of the carbon nanotube may become uneven, and this prevents the formation of a clean film. A particle size below 50 nm is preferred. When forming fine particles of metal or alloy for the catalytic layer 3 by heating and supplying inert gas at the same time, the particles can be made finer as the heating temperature is increased. However, if the particle size is smaller than 0.5 nm, the aggregating force of the particles becomes
20 so strong that the size of the particles in the aggregated parts thereof may become even greater, and it becomes difficult to control the particle size below 0.5 nm and make the particle size uniform at the same time. This leads to a reduction in productivity.

Therefore, the particle size is preferred to be between 0.5 nm and 50 nm. The process of preparing the metallic or alloy particles for the catalytic layer 3 described above will be
25 referred to as "preprocessing" hereinafter.

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The optimum heating temperature in the preprocessing may vary depending on the kind of metal or alloy that is used in the catalytic layer 3. As will be discussed in connection with preferred embodiments, when the catalytic layer 3 is made of iron (Fe), the optimum heating temperature would be approximately 700 °C (973 °K). This
5 temperature in absolute (Kelvin) temperature is approximately 0.54 times the melting point of iron or 1808 °K (1536 °C), and is substantially equal to the temperature from which the atoms become able to move freely in solid (first recrystallization temperature). Thus, the optimum heating temperature for turning the metal or alloy for the catalytic layer into fine particles is in the vicinity of 0.54 T_m (0.54 T_m ± 0.05T_m) where T_m is
10 the melting point of the metal or alloy in absolute temperature.

When the preprocessing is concluded, in step 5, the flow rate of the inert gas is reduced, and material gas (hydrocarbon gas) such as acetylene, methane and ethylene is introduced into the tube at a prescribed flow rate. This causes a carbon nanotube having a diameter in the range of 0.5 to 100 nm to grow on the electroconductive layer 2, for
15 instance, in the form of a carbon nanotube film 5 having a thickness in the range of 0.01 μm to 300 μm (Figure 2e). The produced carbon nanotube film 5 is generally oriented perpendicularly with respect to the assembly 4 or the substrate 1, and demonstrates a favorable electroconductivity in this direction. The material gas generates hydrogen as the carbon nanotube is produced, and the hydrogen along with the excess gas
20 (hydrocarbon) that was not used is expelled from the other end (right end in Figure 3) of the quartz tube 12.

During the process of forming the carbon nanotube, if the flow rate of the material gas is excessive, amorphous carbon other than carbon nanotube or soot is produced, and this prevents the growth of the carbon nanotube resulting in a reduction
25 of the content of the carbon nanotube in the film 5. Conversely, if the flow rate of the

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material gas is inadequate, the growth of the carbon nanotube is reduced resulting in a poor productivity. The flow rate ratio of the material gas to the carrier gas (inert gas) is preferably from 1/2 to 1/50, and more preferably approximately 1/10.

The flow velocity of the mixed gas consisting of the inert gas and material gas
5 along the surface of the assembly 4 also affects the formation of the carbon nanotube film 5. If the flow velocity is too small, soot is actively produced and the content of the carbon nanotube in the film 5 decreases. If the flow velocity is excessive, much of the material gas is expelled without contributing to the formation of the carbon nanotube, and the productivity is impaired. A flow rate in the range of 1 cm/minute to 100
10 cm/minute is preferred, and a flow rate in the range of 30 cm/minute to 40 cm/minute (corresponding to approximately 200 to 300 sccm when the inner diameter of the tube is 30 mm) is particularly preferred. A flow rate of approximately 30 cm/minute (corresponding to approximately 200 sccm when the inner diameter of the tube is 30 mm) is most preferred.

15 During the process of forming the film, by keeping the flow rate of the material gas and carrier gas (inert gas) constant, the carbon nanotube can be made to grow vertically with respect to the substrate. By slightly varying the flow rate, the carbon nanotube can be made to grow in a curved manner. Curving the carbon nanotube promotes the entangling of the carbon nanotube fibers, and this in turn increases the
20 firmness of the carbon nanotube film 5 and develops electroconductivity in lateral directions.

When the formation of the film is concluded, in step 6, the introduction of the material gas is terminated and the assembly is allowed to cool to the room temperature by continuing the flow of the inert gas. In step 7, the assembly 4 having the carbon
25 nanotube film 5 formed thereon is removed from the electric furnace 16 and is

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processed by a high temperature in the atmosphere so that the amorphous carbon and the part of the carbon nanotube containing a large number of defects are selectively eliminated by oxidization and numerous gaps is produced in the carbon nanotube film 5. The part of the carbon nanotube having a substantially perfect crystalline configuration is resistant to oxidization and thereby remains unaffected. By suitably controlling the oxidization process, the density of the carbon nanotube fibers can be adjusted. The density of the carbon nanotube fibers may be in the order of 1,000 to 10^{12} fibers/mm². The agent for the oxidization may also consist of gas containing oxygen at a prescribed partial pressure or heated nitric acid as well as atmosphere.

Thus, according to the present invention, a large number of metallic or alloy particles 3a can be formed by heating the metal or alloy in the catalytic layer 2 formed on the electroconductive member (electroconductive layer) 2 at a prescribed temperature while supplying inert gas. The carbon nanotube film 5 can be formed on the electroconductive member 2 in a favorable manner by growing carbon nanotube film 5 with the aid of the metallic or alloy particles 3a serving as a catalyst. For the formation of the carbon film, thermal CVD (which is also called as the chemical vapor deposition or chemical gas-phase growth method) was used in the foregoing embodiment, but other methods such as the microwave plasma method (plasma CVD), laser vapor deposition and sputtering can be also used.

When the carbon nanotube film 5 formed on the electroconductive member 2 as described above is used in a fuel cell, a catalyst such as platinum is deposited on the carbon nanotube film 5 and an electrolyte layer is placed thereon. Therefore, when the carbon nanotube film 5 is used in a fuel cell, the separator (inorganic substrate 1), electrode (electroconductive layer 2 and carbon nanotube film 5), platinum catalyst and electrolyte can be formed one over the other in a continuous matter and the interfaces

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between these layers can be formed highly neatly. Therefore, as opposed to the conventional fuel cell, there is no need to apply an external force to the film/electrode assembly (MEA) by using threaded bolts or the like for the purpose of reducing the contact resistance on the surface of the electrode, and the interface resistance can be minimized in a stable manner. Because the interface resistance can be minimized both easily and reliably, the production management can be simplified and the productivity can be improved. Also, the elimination of the threaded bolts or other means for applying an external force allows the size of the fuel cell to be minimized. Also, using the carbon nanotube film 5 in the fuel cell provides the following advantages. (1) The overall resistance of the fuel cell can be minimized because the carbon nanotube film can be formed as a thin film without any difficulty. (2) Because the hydrophobic property that is required for the oxygen electrode is produced on the surface of the carbon nanotube surface, the property of the fuel cell is prevented from being prematurely degraded by the clogging of the pores with water. (3) Because the carbon nanotube having a relatively high crystalline configuration is resistant to corrosion, the service life of the fuel cell can be extended. (4) Because the carbon nanotube is highly porous, it serves as an excellent gas diffusion layer which favorably permits transmission of gas such as hydrogen and oxygen and offers a large surface area for adequately promoting the reaction.

20 With reference to the schematic sectional view of Figure 4, another embodiment of the method for forming a carbon nanotube according to the present invention is described in the following. The device illustrated in Figure 3 was used for the film forming process.

 A silicon substrate 21 having a mirror finished surface is cleansed in sulfuric acid - hydrogen peroxide for 10 minutes, and is then rinsed in water. Oxide film thereon

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is removed by using buffered hydrofluoric acid (MHF) and is dried (Figure 4a). Titanium (Ti) film 22a is formed on the cleansed silicon substrate 21 to a thickness of 50 nm at the rate of 1 nm/sec under a pressure of 6×10^{-5} Pa by resistive heating vapor deposition, and tungsten (W) film 22b is formed thereon to a thickness of 100 nm under an Ar partial pressure of 5×10^{-3} Torr (6.7×10^{-4} Pa) by RF sputtering (Figure 4b). The RF sputtering is suited for forming film of material having a high melting point such as tungsten. The titanium (Ti) film 22a and tungsten (W) film 22b forms an electroconductive layer 22. Then, under a pressure of 1×10^{-4} Pa, iron (Fe) is deposited on the tungsten film 22b at the rate of 0.1 nm/sec to a thickness of 5 nm so as to form a catalytic layer 23 having a thickness of 5 nm (Figure 4c). Electron beam vapor deposition is suited for forming film of material having a relatively low melting point such as iron. The assembly having the electroconductive layer 22 and catalytic layer 23 formed on the silicon substrate 21 is secured to the quartz holder 14 placed in the quartz tube 12 in the thermal CVD device 10 shown in Figure 3. The inner diameter of the quartz tube 12 is 30 mm. Helium gas is introduced into the quartz tube 12 at the flow rate of 230 sccm, and the temperature of the electric furnace 16 is set to approximately 700 °C. When the temperature of the electric furnace 16 substantially reaches 700 °C, the same temperature is maintained for 5 to 30 minutes so that the iron 23 on the surface of the assembly turns into fine particles 23a (Figure 4d).

Figure 5 includes photographs that show the state of the iron particles 23a when the heating temperature was changed. As shown in Figure 5(a), when the heating temperature was 600 °C which is lower than 700 °C, the iron did not adequately turn into fine particles. As shown in Figure 5(c), when the heating temperature was 800 °C which is higher than 700 °C, the iron particles became coarse and failed to turn into adequately fine particles. According to the present embodiment, the iron on the surface

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turned into fine particles in an optimum fashion when the heating temperature was 700 °C. Thus, according to the present invention, the heating temperature of 700 °C was most desirable in obtaining fine particles for the catalytic layer 23. However, how the catalytic metal turns into fine particles very much depends on the thickness of the catalytic layer 23, wettability of the lower electroconductive layer 22, configuration of the electroconductive layer 22 and heating time, and the optimum temperature may well depend on such factors.

After the iron of the catalytic layer 23 turns into small particles, acetylene (C_2H_2) is introduced into the tube at the flow rate of 30 sccm while the flow rate of helium is reduced to 200 sccm. After about fifteen minutes of processing, a multi-walled nanotube (MWNT) 25 having a thickness of approximately 30 μm is obtained (Figure 4e). Thereafter, the supply of acetylene is terminated and the assembly is cooled to the room temperature by flowing helium. The assembly 24 having the MWNT 25 formed thereon is removed from the tube, and amorphous carbon is removed by processing the assembly in the atmosphere for five minutes at the temperature of 700 °C. This produces a carbon nanotube structure having numerous gaps therein. The produced carbon nanotube consists of MWNT having a diameter in the range of 10 to 50 nm and the film is formed by fibers extending perpendicularly to the substrate.

Thus, according to the present invention, the metal or alloy of the catalytic layer can be turned into fine particles both easily and reliably by first forming the catalytic layer consisting of the metal or alloy serving as a catalyst for forming a carbon nanotube on an electroconductive member and then keeping it at a prescribed temperature while supplying inert gas, and the catalytic particles prepared in this manner allow the carbon nanotube to be formed on the electroconductive member in an efficient manner.

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Although the present invention has been described in terms of preferred embodiments thereof, it is obvious to a person skilled in the art that various alterations and modifications are possible without departing from the scope of the present invention which is set forth in the appended claims.

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CLAIMS

1. A method for making a carbon nanotube on an electroconductive member,
comprising the steps of:
 - 5 forming a catalytic layer including a metal or alloy that serves as a catalyst for
growing a carbon nanotube on the electroconductive member;
processing the metal or alloy of the catalytic layer so as to turn it into small
particles; and
growing a carbon nanotube on the electroconductive member by using the
10 small particles of the metal or alloy of the catalytic layer as a catalyst;
wherein the step of processing the metal or alloy of the catalytic layer so as to
turn it into small particles comprises the step of heating the catalytic layer formed on the
electroconductive member to a prescribed temperature while supplying inert gas.
- 15 2. A method for making a carbon nanotube according to claim 1, wherein the
catalytic layer comprises a member selected from a group consisting of Fe, Ni, Co, Mo
and an alloy thereof.
3. A method for making a carbon nanotube according to claim 1, wherein the
20 electroconductive member comprises at least one material selected from a group
consisting of Ti, Au, Ni, Co, Cu, Al, Mo, W and Ta.
4. A method for making a carbon nanotube according to claim 1, wherein the
inert gas consists of helium or argon.

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5. A method for making a carbon nanotube according to claim 1, wherein the prescribed temperature is in range of $0.49T_m$ to $0.59T_m$ where T_m is the melting point of the metal or alloy of the catalytic layer in Kelvin.
- 5 6. A method for making a carbon nanotube according to claim 5, wherein the catalytic layer is made of iron, and the prescribed temperature is approximately 700 °C.
7. A method for making a carbon nanotube according to claim 1, wherein the small particles of the metal or alloy have a particle size of 0.5 to 50 nm.
- 10 8. A method for making a carbon nanotube according to claim 1, wherein the step of growing the carbon nanotube comprises the step of supplying mixed gas containing hydrocarbon gas and the inert gas at a ratio of 1:2 to 1:50.
- 15 9. A method for making a carbon nanotube according to claim 8, wherein the step of supplying the mixed gas is conducted at a flow rate of 1 to 100 cm/min.
10. A method for making a carbon nanotube according to claim 9, wherein the step of supplying the mixed gas is conducted at a flow rate of approximately 30 cm/min.
- 20 11. A method for making a carbon nanotube according to claim 9, wherein the step of growing the carbon nanotube comprises the step of placing the electroconductive member including the small particles of the metal or alloy in a tube having an inner diameter of approximately 30 mm, and flowing the mixed gas substantially along the
- 25 length of the tube at a flow rate of 200 to 300 sccm (standard cubic centimeter per

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minute).

12. A method for making a carbon nanotube according to claim 1, wherein the electroconductive member comprises an inorganic substrate.

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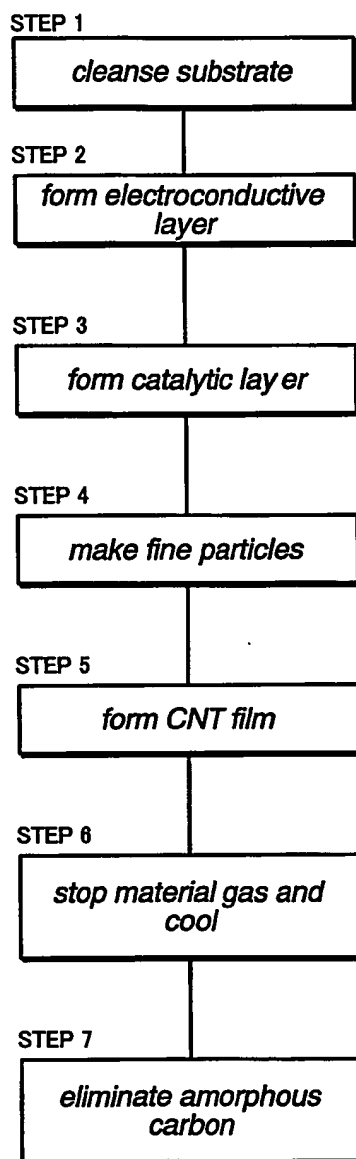
Fig.1

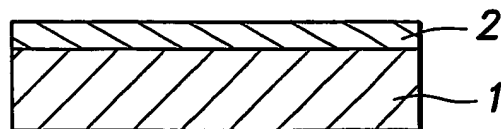
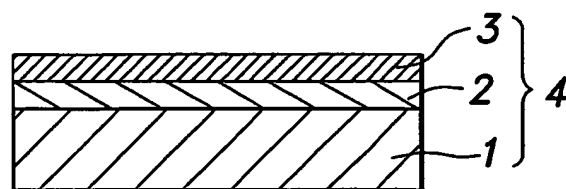
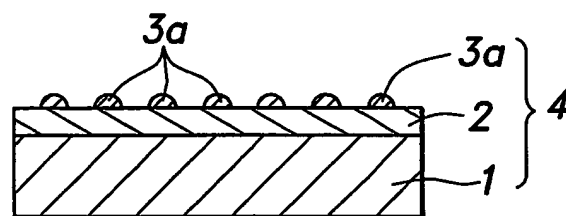
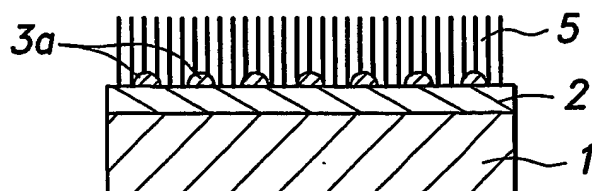
Fig.2a*Fig.2b**Fig.2c**Fig.2d**Fig.2e*

Fig.3

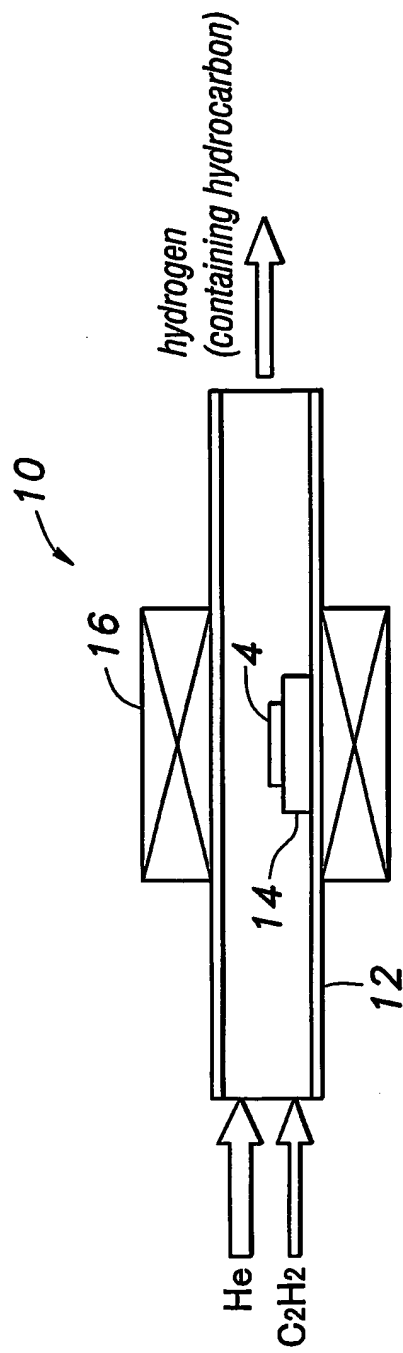


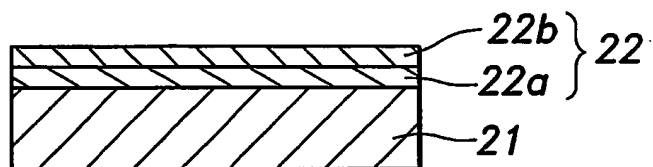
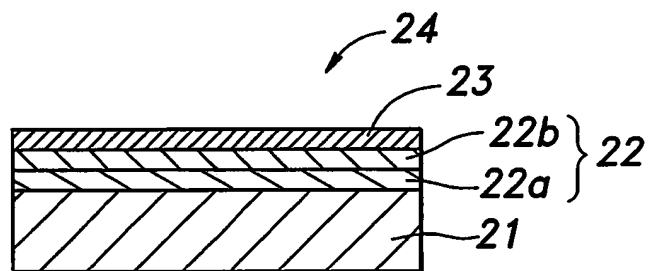
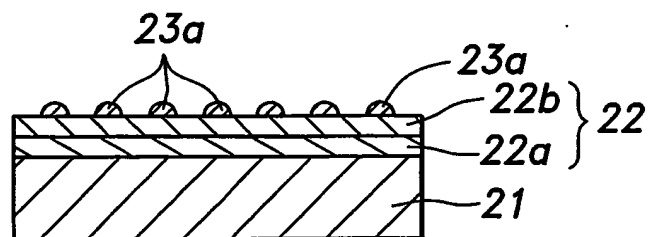
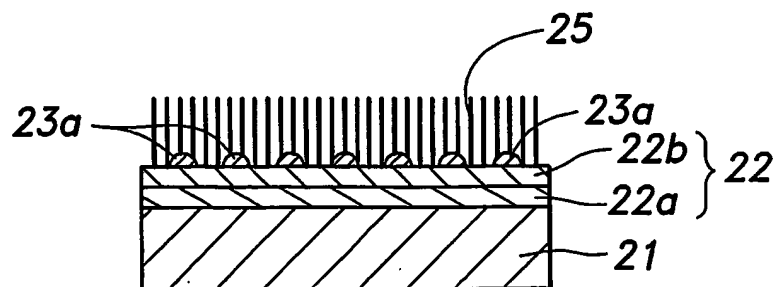
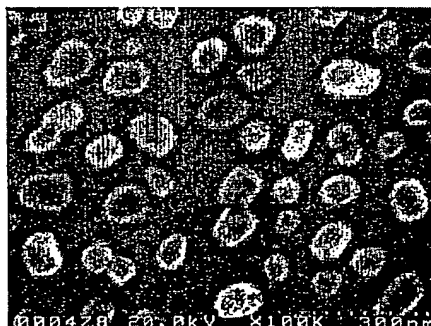
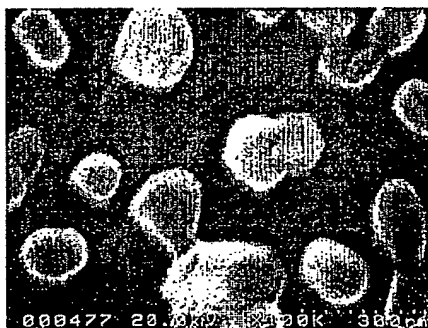
Fig.4a*Fig.4b**Fig.4c**Fig.4d**Fig.4e*

Fig.5a*Fe particles processed
at 600 °C**Fig.5b**Fe particles processed
at 700 °C**Fig.5c**Fe particles processed
at 800 °C*

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/05628

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/02 B01J23/28 B01J23/745 B01J23/75 B01J23/755
 B01J35/02 B01J37/08 B01J37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEN X. H. ET AL: "The formation conditions of carbon nanotubes array based on FeNi alloy island films" THIN SOLID FILMS, 1999, pages 6-9, XP002254581 "Experiment" figure 2	1,2,5, 7-9,12
X	US 2002/055010 A1 (GAO YUFEI ET AL) 9 May 2002 (2002-05-09) paragraph '0019! - paragraph '0023!	1-6
X	EP 1 129 990 A (LUCENT TECHNOLOGIES INC) 5 September 2001 (2001-09-05) paragraph '0017! - paragraph '0027!; figure 2	1,2
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search

16 September 2003

Date of mailing of the international search report

01/10/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/05628

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 062 931 A (WANG WEN-CHUN ET AL) 16 May 2000 (2000-05-16) column 3, line 39 -column 4, line 37 -----	1
P,X	EP 1 251 543 A (VA TECH TRANSMISSION & DISTRIB) 23 October 2002 (2002-10-23) paragraph '0013! - paragraph '0016! paragraph '0019!; example 1 -----	1-3,5,7, 12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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